ISSN 1070-4280, Russian Journal of Organic Chemistry, 2007, Vol. 43, No. 9, pp. 1413–1414. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © O.V. Surikova, A.G. Mikhailovskii, N.N. Polygalova, P.G. Neifel'd, M.I. Vakhrin, 2007, published in Zhurnal Organicheskoi Khimii, 2007, Vol. 43, No. 9, pp. 1416–1418.

SHORT COMMUNICATIONS

Synthesis of 1-[2-(1,3-Benzoxazol-2-yl)-2-oxoethylidene]-3,3-dimethyl-1,2,3,4-tetrahydroisoquinoline Derivatives

O. V. Surikova, A. G. Mikhailovskii, N. N. Polygalova, P. G. Neifel'd, and M. I. Vakhrin

Perm State Pharmaceutical Academy, ul. Lenina 48, Perm, 614990 Russia
e-mail: perm@pfa.ru

Received January 30, 2007

DOI: 10.1134/S1070428007090278

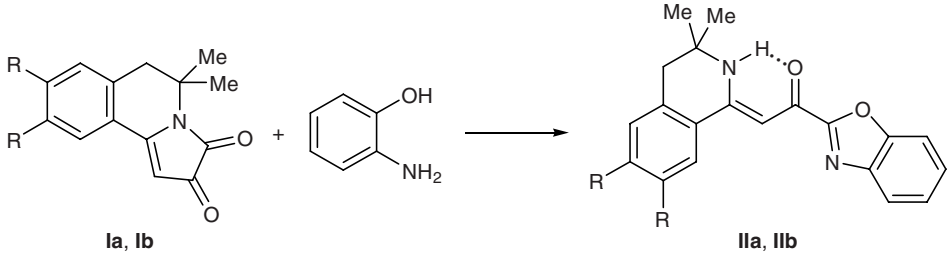
2,3-Dioxopyrrolo[2,1-*a*]isoquinoline derivatives are chemically active compounds whose molecules possess several reaction centers [1–3]. Diversity of their properties makes them promising as intermediate products in the synthesis of alkaloid analogs and other fused systems. While continuing studies in this line we have found that reactions of compounds **Ia** and **Ib** [4] with *o*-aminophenol involve opening of the dihydropyrrole ring to produce enamino ketones **IIa** and **IIb**, respectively.

It is known that acylation of aromatic amines with compounds **Ia** and **Ib** requires acid catalysis [5]. However, their reaction with *o*-aminophenol occurs in the absence of an acid. Presumably, the process is catalyzed by fairly acidic phenolic hydroxy group. Moreover, the formation of aromatic benzoxazole system is favorable from the viewpoint of energy.

Compounds **IIa** and **IIb** may be regarded as new potential synthons [6] containing isoquinoline and benzoxazole rings in a single molecule; such derivatives have been almost unknown previously. The described reaction offers new facilities in the field of their synthesis and application.

1-(1,3-Benzoxazol-2-yl)-2-(3,3-dimethyl-1,2,3,4-tetrahydroisoquinolin-1-ylidene)ethanone (IIa). A solution of 2.27 g (0.01 mol) of compound **Ia** and 1.64 g (0.015 mol) of *o*-aminophenol in 50 ml of propan-2-ol was heated for 1 h under reflux (the progress of the reaction was monitored by TLC); during the process, the originally red solution turned yellow. The mixture was cooled to 20°C and diluted with 150 ml of water, and the precipitate was filtered off, dried, and recrystallized from acetonitrile. Yield 2.4 g (75%), light red crystals, mp 214°C. IR spectrum, ν, cm^{-1}: 1625, 3050 (C=O···H–N). ^1H NMR spectrum, δ, ppm: 1.39 s (6H, CH_3), 2.88 s (2H, CH_2), 6.38 s (HC=), 6.97–7.83 m (8H, H_{arom}), 11.60 s (NH). ^{13}C NMR spectrum, δ_C, ppm: 28.32 (CH_3, J = 123.2 Hz), 41.76 (C^4, J = 128.2 Hz), 50.04 (C^3), 84.79 (HC=, J = 164.8 Hz), 116.05 (C^8, J = 163.1 Hz), 124.98 (C^6, J = 162.8 Hz), 124.88 (C^7, J = 163.9 Hz), 125.24 (C^5, J = 163.1 Hz), 128.85 and 132.60 (C^{4a}, C^{8a}), 153.79 ($C^{2'}$), 144.34 ($C^{3a'}$), 150.42 ($C^{7a'}$), 125.50 ($C^{4'}$, J = 159.9 Hz), 160.49 ($C^{5'}$, J = 160.5 Hz), 128.79 ($C^{6'}$, J = 157.2 Hz), 130.74 ($C^{7'}$, J = 161.5 Hz), 138.88 (C^1), 155.13 (C=O). Mass spectrum, m/z (I_{rel}, %): 318 (100) $[M]^+$, 303 (93) $[M - CH_3]^+$. Found, %: C 75.32; H 5.62; N 8.91. $C_{20}H_{18}N_2O_2$. Calculated, %: C 75.45; H 5.70; N 8.80.

1-(1,3-Benzoxazol-2-yl)-2-(6,7-dimethoxy-3,3-dimethyl-1,2,3,4-tetrahydroisoquinolin-1-ylidene)-



Ia, **Ib** **IIa**, **IIb**

R = H (**a**), MeO (**b**).

ethanone (IIb) was synthesized in a similar way. Yield 2.28 g (60%), light red crystals, mp 198°C. IR spectrum, ν, cm^{-1}: 1620, 3050 (C=O···H–N). ^1H NMR spectrum, δ, ppm: 1.38 s (6H, CH_3), 2.79 s (2H, CH_2), 3.87 s and 3.91 s (3H each, CH_3O), 6.26 s (HC=), 6.57–7.31 m (6H, H_{arom}), 11.60 s (NH). Mass spectrum, *m*/*z* (I_{rel}, %): 378 (100) $[M]^+$, 363 (87) $[M - CH_3]^+$. Found, %: C 69.72; H 5.68; N 7.53. $C_{22}H_{22}N_2O_4$. Calculated, %: C 69.83; H 5.86; N 7.40.

The IR spectra were recorded from solutions in chloroform (*c* = 0.01 M) on a Specord M-80 spectrometer. The ^1H and ^{13}C NMR spectra were measured from solutions in $CDCl_3$ on a Bruker 300 instrument (300 MHz for ^1H). The mass spectra (electron impact, 70 eV) were run on a MAT-311 mass spectrometer.

REFERENCES

1. Polygalova, N.N., Mikhailovskii, A.G., and Vakhrin, M.I., *The Chemistry and Biological Activity of Synthetic and Natural Compounds: Nitrogen-Containing Heterocycles*, Kartsev, V.G., Ed., Moscow: ICSPF, 2006, vol. 1, p. 402.
2. Mikhailovskii, A.G. and Shklyaev, V.S., *Khim. Geterotsikl. Soedin*., 1997, p. 291.
3. Polygalova, N.N. and Mikhailovskii, A.G., *Khim. Geterotsikl. Soedin*., 2005, p. 1383.
4. Shklyaev, V.S., Aleksandrov, B.B., and Mikhailovskii, A.G., *Khim. Geterotsikl. Soedin*., 1987, p. 963.
5. Polygalova, N.N. and Mikhailovskii, A.G., *Khim. Geterotsikl. Soedin*., 2005, p. 1378.
6. Granik, V.G., *Organicheskaya khimiya* (Organic Chemistry), Moscow: Vuzovskaya Kniga, 2003, p. 171.